Dual Phase Membrane for High temperature CO_2 Separation

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ABSTRACT

Dual-phase membranes consisting of stainless steel supports infiltrated with molten carbonate have been shown to be selective to CO_2 at high temperatures (400-650°C). However, over time at high temperatures, the formation of iron oxides on the surface of the stainless steel supports render the membranes ineffective. This report details synthesis and characteristics of dual-phase carbonate membrane with an oxidation resistant perovskite type ceramic (lanthanum-strontium-cobaltite-iron; LSCF) support. Porous LSCF supports were prepared from its powder synthesized by the citrate method. Both steady state permeation and mercury porosimetry confirmed that the LSCF membrane sintered at 900^{o}C has pores large enough to absorb molten carbonate, yet small enough to retain the molten carbonate under high pressure conditions. Results of XRD analysis have shown that LSCF and the molten carbonate mixture do not react with each other at temperatures below 700^{o}C. Four-point method conductivity tests indicate that the support material has sufficiently high electronic conductivity for this application. Li-Na-K carbonate was coated to the porous LSCF support by a liquid infiltration method. Helium permeance of the support before and after infiltration of molten carbonate are on the order of 10^{-6} and 10^{-10} moles/m^2·Pa·s respectively, indicating that the molten carbonate is able to sufficiently infiltrate the membrane. Preliminary high temperature permeation experiments indicate that the membrane does separate CO_2 in the presence of O_2, with a maximum flux of 0.623 ml/cm^2·min obtained at 850°C.

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INTRODUCTION

The previous annual report focused on past efforts that combined the use of a porous, electronically conductive, stainless steel supports infiltrated with molten carbonate (Li_2CO_3, K_2CO_3, and Na_2CO_3) to produce a dual-phase membrane for high temperature CO_2 separation. Additionally, the report also touched on early efforts to determine whether or not lanthanum cobaltite ($LaCO_3$) doped with Strontium (Sr) and Iron (Fe) would be a viable candidate for use as the support for the dual-phase membrane.

Briefly recall, in the presence of an election, CO_2 and O_2 will react with electrons to form carbonaceous, CO_3^{2-}, as shown in the following reaction:

$$CO_2 + \frac{1}{2}O_2 + 2e^- \longleftrightarrow CO_3^{2-} \qquad \text{(A)}$$

Separation is driven by the partial pressure gradient of CO_2 between the up and downstream sides of the membrane. Once CO_3^{2-} reaches the downstream side of the membrane, the electrons are released back into the metal support and circulated toward upstream side of the membrane. CO_3^{2-} ion decomposes on the downstream side to release CO_2 and O_2.

The stainless steel dual-phase membrane was found to separate CO_2, with a maximum flux of about 0.177 ml/cm^2·min at 650°C. However, XRD results indicated that $LiFe_5O_8$ and $LiFeO_2$ began to form on the surface of the support at high temperature [1]. Both materials are insulators [2], thus separation was inhibited by the presence these compounds on the surface. Accordingly, efforts have shifted toward the use of electronically conductive ceramic materials to avoid problems involving oxidation. This remainder of this report will detail the synthesis and characterization of a lanthanum-strontium-cobalt-iron (LSCF) perovskite material for use as the support for the dual-phase membrane.

EXPERIMENTAL

LSCF ceramic powder was prepared via the citrate method. To form the porous support for the dual phase membrane, the LSCF powder was pressed into disk form. The resulting disk was sintered at 900°C for 24 hours. The porous LSCF membranes were infiltrated with a Li/Na/K molten carbonate to obtain the dual-phase membrane. The infiltration procedure was done according to Chung, et al., [1] with minor adjustments to account for the difference in material.

The pore-size and pore-size distribution of the supports was measured by using steady state helium permeation and mercury porosimetry. The phase structure and stability of the support material with molten carbonate was characterized by XRD from 300-600°C. Electronic conductivity of LSCF sintered at 900°C was measured by the four-point DC method. Conductivity measurements were obtained at low oxygen partial pressure (PO_2 = 10^{-4} atm) from 300-700°C.

RESULTS AND DISCUSSION

The first objective was to determine the permeance and pore diameter of the uninfiltrated LSCF supports. Unsteady state helium permeance was found to be on the order of 10^{-6} moles/m^2·Pa·s. Based on the results shown in Figures 1 and 2, steady state helium permeance and mercury porosity measurements both indicated that the average pore diameter was approximately 330 nm.

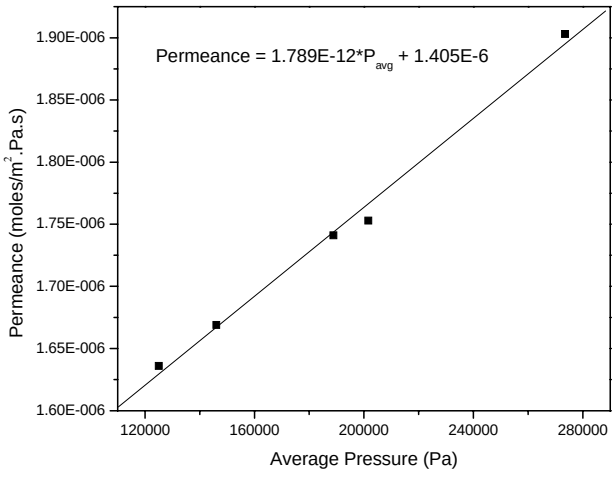

Figure 1: Steady state permeation results for LSCF membrane

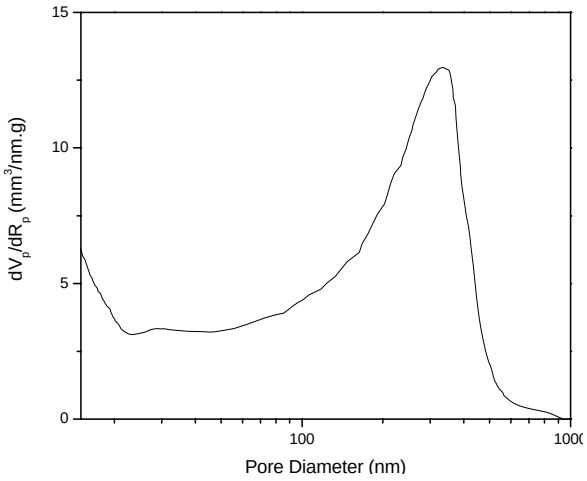

Figure 2: LSCF pore size distribution From mercury porosimetry

The results show that the pores are large enough to allow for infiltration of molten carbonate, yet small enough to retain the molten carbonate under high pressure conditions [1].

Electronic conductivity of the supports was measured by the four-point DC method. Figure 3 shows conductivity of the support as a function of temperature.

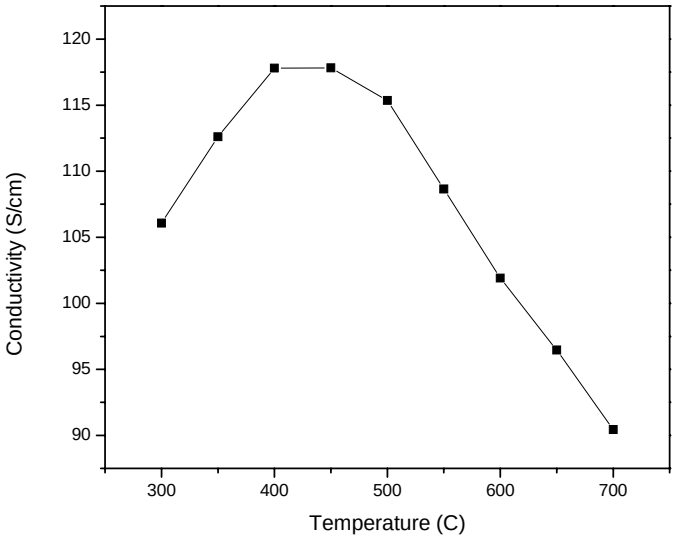

Figure 3: Conductivity of LSCF sintered at 900°C as a function of temperature

The trend shown in the figure matches that of the trends reported by Xu et al. [3]. However, values reported in this work are about an order of magnitude less than those in their work. It is believed that the porosity, as a result of the lower sintering temperature, is the cause of the decrease in electronic conductivity. Nevertheless, the conductivity of the LSCF support is sufficiently high for use as the electron conducting phase for the dual-phase membrane.

Figure 4 shows the XRD results of the stability tests conducted on the 50/50 weight-percent mixture of LSCF and molten carbonate in air for 48 hours. The results indicate that there is no change in phase of the LSCF powder below 600°C.

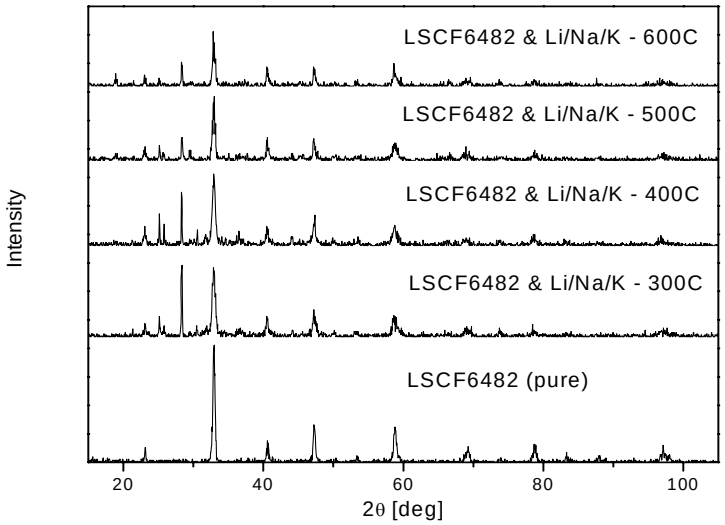

Figure 4: XRD results of LSCF/molten carbonate mixtures from 300-600°C

Peaks at 25.2C° and 28.4° in the LSCF + Li/Na/K XRD scans represent the carbonate contributions. As can be seen, there is little change between the pure LSCF scan at room temperature and those done between 300-600°C, indicating the lack of phase change. Further stability testing is required from 700-900°C to determine whether or not the structure remains in tact.

Finally, the permeance of the infiltrated membranes was tested to ensure complete infiltration of molten carbonate into the support. Several LSCF supports were infiltrated with molten carbonate at 550°C. Recall that prior to infiltration, the permeance of the supports was 10^{-6} moles/m^2·Pa·s. After infiltration, unsteady state helium permeance decreased by four orders of magnitude to 10^{-10} moles/m^2·Pa·s. This value matches the permeance values of the infiltrated supports for the stainless steel membranes in the previous work [1]. The low value for the permeance indicates that the membrane is dense.

All results obtained indicated that LSCF would be a viable candidate for use as a support material for the dual-phase membrane. The next step in the process was to test the

LSCF dual-phase membrane at high temperature. Originally, the idea was to use graphite gaskets to seal the membrane. However, this was found to be a problem for two reasons. First, the graphite gaskets required a great deal of compression to form a seal. This posed a problem, as the ceramic membrane, while mechanically stable, was unable to withstand the amount of compression required to form an adequate seal. Secondly, even if the membrane would seal, the graphite gasket would not last long at high temperature in the presence of oxygen. As a result, a new method to test the dual phase membrane at high temperature was sought.

A high temperature permeation apparatus present in the ASU lab was seen as a suitable alternative. Figure 5 provides a visual description of the apparatus.

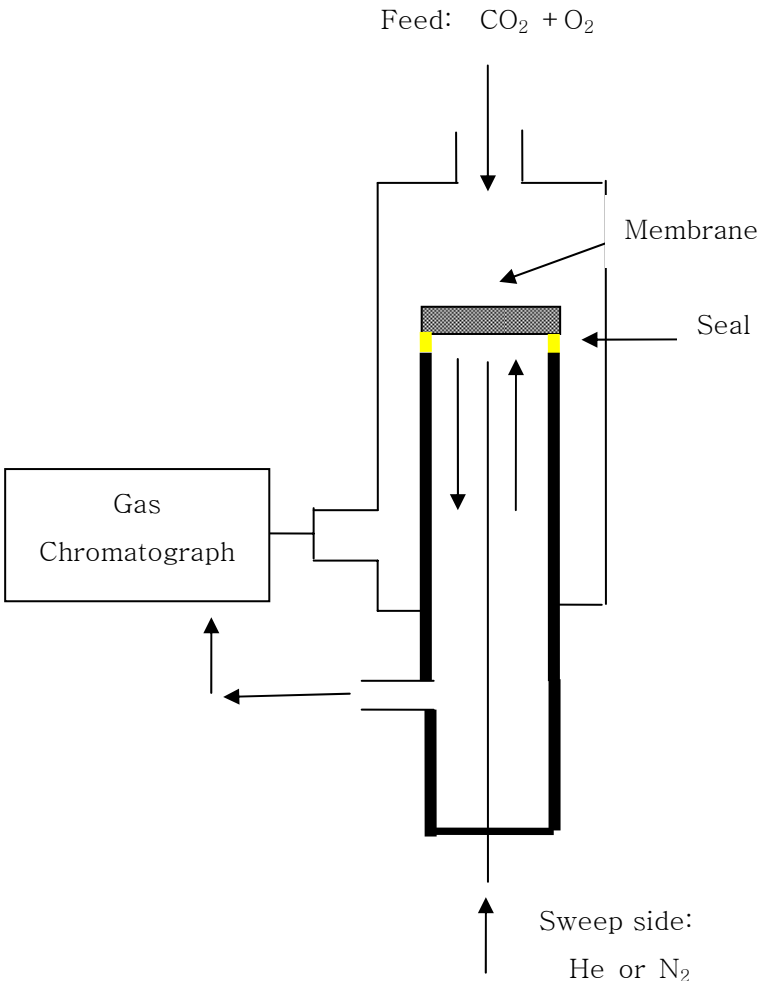

Figure 5: High Temperature Permeation Apparatus for High Temperature CO_2 Separation

The membrane was sealed with a mixture of LSCF powder (40 wt%), ground Pyrex beaker glass (50%), and $NaAlO_2$ (10%). The mixture was ground in a mortar and pestle and mixed with water to form a 'ketchup-like' consistency. The seal material was applied to the outside ring of a quartz tube and an infiltrated LSCF membrane was pressed to form a seal. More sealing material was applied to the outside of the membrane/tube interface to produce a suitable seal. The seal must be heated to 900°C in order for the glass in the mixture to soften.

In a high temperature test, an infiltrated LSCF membrane was heated to 915°C at a ramp rate of 1C/min. In order to protect the membrane (i.e., inhibit the decomposition of carbonates) during heating, CO_2 was fed at a rate of 50 mL/min on both the feed and permeate sides. After remaining at 915°C for approximately 1 hr, the temperature of the system was cooled and high temperature permeation experiments were conducted at 750, 800 and 850°C. For this particular set of experiments, CO_2, He and O_2 were fed at a rate of 100 mL/min, while the sweep rate of N_2 was also maintained at 100 mL/min. The results of the tests are shown in Table 1.

Table 1: High Temperature Permeation Results for LSFC Dual-Phase Membrane

Temperature (°C)	CO_2 flux (in He) (mL/cm^2·min)	CO_2 flux (in O_2) (mL/cm^2·min)
750	0.208	0.317
800	0.508	0.623
850	0.463	0.587

The table shows a considerable CO_2 flux through the dual phase membrane. The CO_2 flux is higher with the presence of oxygen. These results show the ceramic phase provides pathway for oxygen ion and electronic conduction, allowing CO_2 to permeate in the form of $CO_3^{=}$. Additional high temperature permeation tests are underway to find ways to enhance

separation. Such steps as increased feed rate of CO_2, increased sweep rate of N_2 (or He) and increase CO_2 on the feed and permeate site will be examined to optimize separation. Furthermore, additional materials that can be used for the support in the dual-phase membrane will also be investigated in the coming year.

CONCLUSION

Characterization of the LSCF supports showed that the material is suitable for use as the support of the dual-phase membrane. The average pore diameter based on steady state helium permeance measurements and mercury porosimetry was found to be 330nm. Conductivity of the LSCF material was found sufficiently high for this particular application. Furthermore, the LSCF-molten carbonate system was found to be stable between 300 and 600°C, but further tests are required to check the stability at even higher temperatures. Finally, preliminary high temperature permeation data does show that the LSCF-dual phase membrane does, in fact, separate CO_2 when O_2 is present in the feed, with a maximum flux of 0.623 ml/cm^2·min obtained at 850°C. Additional experiments are required to optimize the level of separation achieved.

PUBLICATIONS:

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